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Determination of Organic Contaminants by the Grob Closed-Loop-Stripping Technique

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16. ABSTRACT

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Determination of organic contaminants by the Grob closed-loop-stripping technique

EPA-600/J-81-004
Journal Article

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A modified Grob closed-loop-stripping device is currently being used to concentrate organic contaminants from drinking water. The identification and quantification of organic contaminants at the nanogran per litre (part-per-trillion) level are accomplished by a computerized glass capillary gas chromatography–mass spectrometry system. Applications of closed-loop-stripping analysis (CLSA) for monitoring water by water utilities, for studying the use and effects of alternative disinfectants in drinking water, and for providing data on the removal of organic contaminants from water by granular activated carbon (GAC) treatment are discussed. An attempt to validate the method using statistical computations is also included.

The exposure evaluation branch of the USEPA's health effects research laboratory (HERL) in Cincinnati, Ohio, is responsible for validating sensitive methods for measuring organic contaminants in drinking water, principally in support of epidemiological studies. Its method of choice at this time is Grob closed-loop-stripping analysis (CLSA). In 1973 in Zürich, Switzerland, Grob[1] reported on CLSA for the measurement of semivolatile, intermediate molecular weight organics in drinking water at the ng/L (ppt) level. Later, in 1974, Bellar[2-4] reported his purge-and-trap method (Bellar VOA) for the analysis of purgeable volatile organics at the μg/L (ppb) level.

Water analysis laboratories in the United States quickly adopted the Bellar VOA method[4-6] using packed gas chromatograph (GC) columns, whereas Western European laboratories adopted the Grob CLSA method, which uses wall-coated-open-tubular (WCOT) glass capillary gas chromatography (GC)[2]. The primary reason for the slow adoption of Grob CLSA in this country was the slow acceptance of state-of-the-art WCOT glass capillary column technology and hardware by US manufacturers. That one US company held the exclusive patent rights to manufacture WCOT capillary columns did not help in this regard, and US laboratories now lag behind their Western European counterparts in the use of (GC)[2] for the separation of environmental pollutants. It is unfortunate that this technological gap in gas chromatography has delayed validation of Grob CLSA by US laboratories.

CLSA has great potential as a monitoring tool for water utilities. Current studies on the use and effects of alternative disinfectants in drinking water and research on the removal of organic contaminants from water by granular activated carbon (GAC) need a sensitive and reproducible method like CLSA. In order to comply with proposed organic control regulations that will specify when GAC should be used, reactivated, or replaced, a sensitive method that measures a wide range of halogenated and other organics is necessary.

This paper discusses the applications of CLSA and attempts to validate the method as described most recently by Grob.[7] A modified CLSA device (a 3.8-L [1-gal] jug), computerized (GC)[2]-MS, and automatic quantitation procedures were used to provide analysis results from repetitive direct injections and repetitive purges of standard compounds from water at the 10–100 ng/L (ppt) level for statistical evaluation. Quantitation by GC-MS on single ions versus total ions of a mass spectrum is briefly discussed.

Historical background of Grob closed-loop-stripping analysis (CLSA)

In the past, activated carbon has been used to monitor organic pollutants in air. For example, White et al.[8] of the National Institute of Occupational Safety and Health (NIOSH) reported in 1970 a standard method to measure the amount of selected solvent vapors in industrial atmospheres. The NIOSH method involves passing a standard 10-L volume of industrial room air through a standardized adsorption tube that is packed with activated carbon. After capping the tube and shipping it back to the laboratory, the activated carbon is removed from the tube and placed in a clean vial with 1 mL of carbon disulfide (CS_2). Of the resulting solution 5 μL are introduced into a gas chromatograph equipped with a packed GC column and a flame ionization detector (FID). All phases of this method have been standardized and the equipment is readily available.

Prior to Grob's development of his CLSA method[1] in 1973, he had had an extensive background in the practical uses of activated carbon and WCOT glass capillary GC columns. It was only natural, then, that he considered the use of activated carbon as an adsorbent for the concentration and analysis of organics in potable water at the ng/L (ppt) level. Grob thoroughly discussed the design and development of his CLSA procedure in his first CLSA paper.[1]

As in the NIOSH air analysis method,[8] Grob uses CS_2 to elute the organics off the activated carbon and gas chromatography to separate the organics in the eluent. Like the Bellar VOA method[2] the Grob CLSA method is a vapor-phase stripping method by which those compounds with appreciable vapor pressure over water are removed from the sample by purging it with a large volume of gas and passing the stripping gas through an adsorption tube. Unlike these vapor-phase methods, the Grob method has achieved a millionfold concentration of most low and intermediate molecular weight organics by using a closed-loop design by which 0.5 L of stripping gas is recycled continuously through the water sample, and the adsorption trap (1.5 mg of selected activated carbon) is extracted with 10 μL of CS_2. Quantitation is achieved by spiking the initial water sample with a series of internal standards, by stripping at 30°C for two hours, and by chromatographing the CS_2 extract on a WCOT (GC)[2] column. Grob reported in this initial CLSA paper the (GC)[2]-MS identification of 62 organics in samples of Lake Zürich water and Zürich potable water, about 60 percent of which came from Lake Zürich.

Grob's second paper[9] on CLSA was dedicated primarily to the application of CLSA to raw and finished drinking water in the area of Zürich. Using (GC)[2]-MS for identification, K. Grob and G. Grob reported the occurrence of 136 organics in area water at the low nanogram per litre range. They demonstrated that gasoline was the major pollutant in Lake Zürich. In these first two CLSA papers[1,9] Grob identified 29 unique alkanes and 34 alkyl-substituted benzenes in Zürich's raw and finished drinking water. In 1975, K. Grob, K. Grob Jr., and G. Grob[10] compared the CLSA method with a new trace organic analysis technique, rapid

liquid extraction. This new method involves the extraction of 1 L of water with 200 μL of pentane. The extract is evaporated down to 3 μL and analyzed by $(GC)^2$.

Grob points out that his two methods complement each other: CLSA is very sensitive for low and intermediate molecular weight apolar organics, whereas rapid solvent extraction is better for heavier compounds. Something that many environmental laboratories have only recently rediscovered was also specified by Grob: solvent extracts of water heavily stress $(GC)^2$ columns because nonvolatile components in the extracts shorten column life; CLSA extracts, however, contain more volatile substances and, therefore, $(GC)^2$ columns may be used over a long period of time without loss of column performance.

In 1976 Grob and Zürcher[7] improved and standardized the CLSA method because many water research laboratories (mostly European) were already using the method routinely to study source pollution and such drinking water treatment techniques as the use of bank filtration, activated carbon adsorption, and alternative disinfection methods. Grob clearly pointed out, as he had in previous papers, the major limitations of CLSA, such as the intermediate volatility and molecular weight range of substances readily measured by the method. Most laboratories using CLSA to measure low-level organics in water are following the standardized method of Grob and Zürcher[7], with slight modifications.

The authors have recorded a total of 16 additional references from seven different laboratories (five European) that have used Grob CLSA to measure 192 unique organics in water. However, a brief tour of European water laboratories would indicate that CLSA is being used daily in many more. By 1976 a comprehensive applications paper had been published by Stieglitz et al[11] in West Germany. They used $(GC)^2$-MS CLSA exclusively to monitor and quantitate 103 organics at three different water utilities on the Rhine River. Their data clearly show some of the effects on the raw water of different treatment techniques such as bank filtration, chlorination, and ozonation. Stieglitz slightly modified Grob's CLSA in order to analyze water from the heavily contaminated Rhine River. In two different stages 2-L samples were stripped at pH 3. After 15 min of stripping, the first activated carbon filter was removed from the loop and a new filter was inserted. Stripping was then continued for an additional two hours and 45 minutes. Each filter was extracted separately and the eluents of filters 1 and 2 were combined prior to $(GC)^2$-MS analysis.

Stieglitz reported a standard deviation of 10 to 15 percent for 24 organics at the 100-ng/L level, a $(GC)^2$-MS detection limit of 0.2 ng/L, and a $(GC)^2$-MS identification limit of 2 ng/L. Interesting organics that Stieglitz reported were 24 halogenated aliphatic compounds, including bis(2-chloroisopropyl) ether, 3-chloropropyl ether, 1,2-dibromoethane, many chlorinated isomers of butane and 1,3-butadiene, 16 chlorinated or brominated benzene compounds (brominated C_1, C_2, and C_3 benzene compounds were produced upon chlorination), and three nitrobenzenes (nitrobenzene, nitrotoluene, and nitrotrifluorobenzene).

Starting in 1976 Giger, in Dübendorf, Switzerland, began publishing a long series of comprehensive application papers on Grob CLSA. Zürcher and Giger[12] reported the occurrence of 70 organics at different points on the Glatt River, using $(GC)^2$-MS. Also in 1976 Giger et al[13] reported the $(GC)^2$-MS analysis of trace-organics, using methylene chloride solvent extraction and Grob CLSA. The complexity of environmental samples and the clear advantage of using $(GC)^2$ are demonstrated in this paper. In 1978 Giger, Molnar, and Wakeham[14] applied Grob CLSA to trace the source of chlorinated volatile hydrocarbons in groundwaters and lake waters in the Zürich area. Tetrachloroethylene, the most dominant chlorinated compound, was shown to originate from tertiary-treated sewage and ground spills. Giger clearly demonstrated that Grob CLSA is an excellent method to trace the source of chlorinated hydrocarbons and substituted aromatic hydrocarbons from industrial point sources.

In 1979 Schwarzenbach et al[15] used Grob CLSA to determine the distribution of tetrachloroethylene and 1,4-dichlorobenzene at various depths in Lake Zürich over a 12-month period. One-litre samples were stripped at 30°C for 90 min and quantitation was achieved by $(GC)^2$-FID peak height measurements. Replicate measurements over the one-year study at the 5-ng/L to 70-ng/L range had relative standard deviations of less than 10 percent, except at the thermocline depth of the lake where concentration gradients were greatest. Using Grob CLSA data, Schwarzenbach was able to conduct an accurate mass balance for 1,4-dichlorobenzene into and out of Lake Zürich. Sewage treatment plants introduced 62 kg/year of 1,4-dichlorobenzene to the lake, whereas the Zürich water utilities removed 1 kg/year.

In 1977 Giger[16] proposed the use of Grob CLSA to measure volatile organics in the marine environment. In 1978 Schwarzenbach et al[17] at Woods Hole Oceanographic Institute, along with the late Max Blumer, conducted an extensive analysis of volatile organics in coastal seawater, using Grob CLSA. Since most volatile organics in seawater are present below the 10-ng/kg range, Schwarzenbach stripped 5-L samples at 35°C in order to have good sensitivity for analysis by electron impact and chemical ionization $(GC)^2$-MS. Reproducibility for 20 selected organics in seawater samples was ±15 to 30 percent. Of the 53 organics that were measured in the coastal waters and in a tidal creek of Cape Cod, Mass., the 20-ng/kg level was

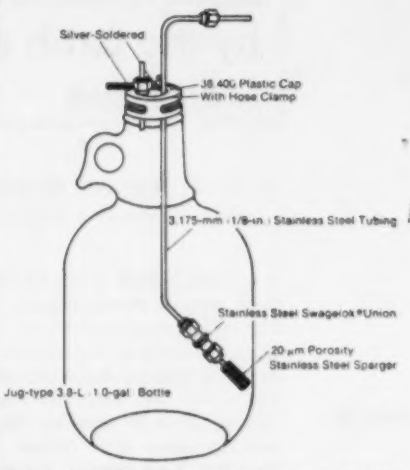

Figure 1. HERL 3.8-L (1-gal) jug sample container

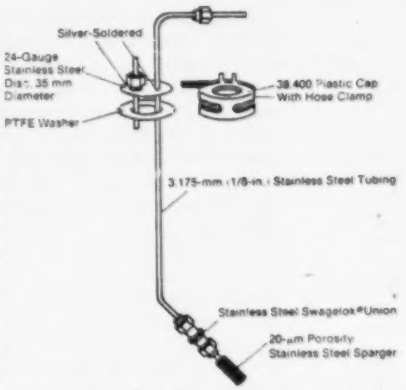

Figure 2. Sparging device for 3.8-L (1-gal) jug sample container

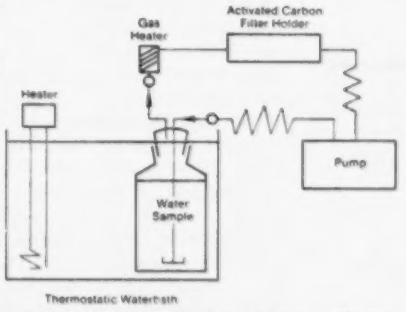

Figure 3. Schematic of closed-loop-stripping apparatus
After Grob and Zürcher[7]

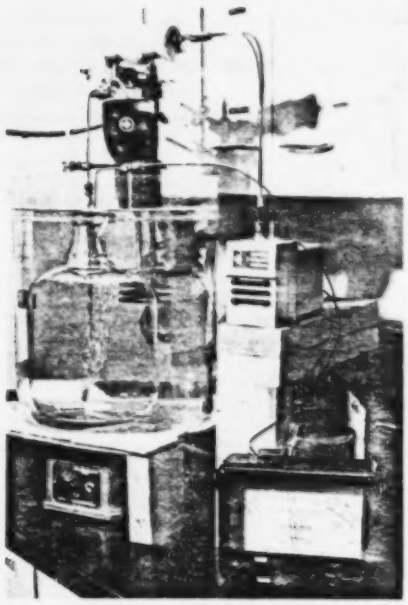

Figure 4. HERL closed-loop-stripping apparatus

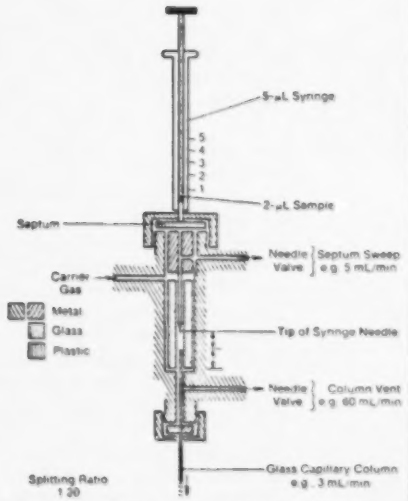

Figure 5. Hot needle injection—Grob-designed injector

only rarely exceeded by a few components. Chronological changes were clearly evident in the CLSA data, owing to petroleum contamination, a phytoplankton bloom, and pollution from recreational activities during the July 4 weekend in 1977.

Reinhard and McCarty at Stanford University have published many papers[19-22] reporting the use of Grob CLSA as one of four analytical methods to assess advanced wastewater treatment processes and the transport of organics from groundwater injection wells. As early as 1976 Reinhard chose four unique analytical methods, because of the complexity of the organics in biologically treated municipal wastewater. Unit processes such as lime treatment, air stripping, recarbonation, chlorination for algae control, filtration, GAC adsorption, reverse osmosis, final chlorination, and groundwater recharge have been thoroughly studied using state-of-the-art analytical methods. Bellar VOA analysis with a packed column GC-electrolytic conductivity detector system was used for haloforms and halogenated compounds with one and two carbons. Grob CLSA was used to quantify compounds of medium volatility and low water solubility. Solvent extraction with two different solvents was used to measure heavier compounds. $(GC)^2$ columns were used on all samples except those analyzed by the Bellar VOA method, and GC-MS was used to confirm all identifications. Reinhard's data clearly indicate the complexity of environmental water samples and the need for sensitive methods such as Grob CLSA and $(GC)^2$.

Experimental methods

Apparatus. The authors have modified the original closed-loop-stripping apparatus of Grob[1] for increased durability and ease of sample handling. With the exception of the sample container, all glass parts have been eliminated and the apparatus constructed of type 304 stainless steel and PTFE; tubing connections are made with Swagelok*† fittings containing PTFE ferrules (Figures 1 and 2).

The sample container is a 3.8-L (1-gal) jug with the neck opening ground flat to ensure a leakproof seal during the vapor-phase stripping. This system allows a sample to be collected and analyzed in the same container. Contamination is minimized, spillage and errors introduced by sample transfer are eliminated, sample changeover is simplified, and the time requirement is greatly reduced. Grob CLSA is accomplished by making the sample vessel, which contains a headspace, part of a closed system in which the entrapped air is continually circulated through the sample and an activated carbon filter (Figure 3). As the air passes through the sample, organic compounds are purged from the water into the headspace air. The filter then adsorbs these compounds from the air.

The HERL closed-loop-stripping apparatus is shown in Figure 4. The water bath temperature is thermostatically controlled at 30°C, and the preheater temperature is maintained at 80°C to prevent condensation of vapors on the carbon filter. The filter holder is insulated from the surrounding atmosphere and its temperature maintained at 40°C.

Sampling and stripping. Water samples are collected directly in muffled (400°C) bottles containing 100 mg of sodium sulfite (Na_2SO_3) to quench residual chlorine and 40 mg of mercuric chloride ($HgCl_2$) to retard bacterial growth. The bottles are filled completely without any headspace and the PTFE-lined caps are applied securely. Samples can be stored at 5°C until analyzed.

In the laboratory, CLSA is initiated by decanting a small amount of the water sample down to the 3.8-L (1-gal) mark, adding 0.6 μL of internal standard solution (1-chloroalkane in acetone), and assembling the purging apparatus. When added to the sample the 0.6 μL of internal standard solution gives a concentration of 52 ng/L each of 1-chlorohexane, 1-chlorooctane, 1-chlorododecane, and 1-chlorohexadecane and 260 ng/L of 1-chlorooctadecane. The larger amount of 1-chlorooctadecane is added because of its poorer recovery efficiency. With a clean, dry, carbon filter in place, the sample is purged by recirculating the headspace for two hours.

Carbon filter extraction. The carbon filter extraction procedure using carbon disulfide is very similar to that used by Grob and others,[1,7,11,13,33] and takes about 10 min to complete. The carbon filter is removed and assembled into the extraction apparatus.[7] The filter is butted up tightly to the receiver tube and secured with a PTFE sleeve. The first 6-μL aliquot of CS_2 is added directly to the top of the carbon and is refluxed back and forth through the carbon three times by alternately cooling the filter with ice to pull the solvent down just below the carbon and warming with the hand to push the solvent back through. When the solvent is pulled through a fourth time, it is transferred to the receiver by swinging the tube in a long downward arc. As most of the solvent aliquot is required to wet the carbon, only about 2-3 μL will be recovered. The process is repeated with three additional aliquots of 2 μL each, which results in a total sample volume of about 8 μL. Of this final volume 2 μL are used for $(GC)^2$ or $(GC)^2$-MS analysis.

$(GC)^2$-MS analyses. All $(GC)^2$-MS analyses, structural identifications, and quantitation for studies reported in this paper were performed on a mass spectrometer* equipped with a data system computer.† A gas chromatograph‡ equipped with a Grob-designed splitless injector[11] and a 60-m × 0.25-mm ID WCOT glass capillary SP2100 column

*Teflon, du Pont de Nemours & Co. Inc., Wilmington, Del.
†Crawford Fitting Co., Solon, Ohio.

*Model 3300, Finnigan Corp., Sunnyvale, Calif.
†Model 2000, INCOS, Finnigan Corp., Sunnyvale, Calif.
‡Model 9500, Finnigan, Finnigan Corp., Sunnyvale, Calif.

TABLE 1

GC-MS analyses of drinking water GAC influents and effluents at time zero and after one month of pilot study

Compounds	Time Zero		Time One Month	
	Influent Concentration ng/L	Effluent Concentration ng/L	Influent Concentration ng/L	Effluent Concentration ng/L
Chloroform*	15	0	34	0.8
1,1,1,-Trichloroethane	3	0	38	2
Benzene	0	0	10	0
Carbon tetrachloride	4	0	58	4
Hexane	0	12	0	0
1,2-Dichloropropane	0	0	21	0
Trichloroethene	5	0	16	0
Bromodichloromethane*	5	0.02	33	0.1
Methylcyclohexane	0	21	0	0
Toluene	29	18	10	5
Dibromochloromethane*	0.7	0	18	0.02
Tetrachloroethane	9	0	23	0
Dichloroiodomethane	20	0	35	0
1,3- and 1,4-Dimethylbenzene	21	13	8	4
Bromoform*	0.02	0	0.8	0
1-Nonene	0	0	0	0
Octanal	0	2	0	14
1,4-Dichlorobenzene	10	0	27	0
1,2-Dichlorobenzene	9	9	11	0
Hexachloroethane	5	0	7	0
Nonanal	2	9	10	42
1,2,4-Trichlorobenzene	8	0	5	0
Decanal	4	10	16	124
Undecanal	0	0	0	7

*Amounts are approximately μg/L (ppb), based on preliminary recovery efficiencies.

TABLE 2A

Compounds prominent in one GC-MS analysis but not the other after one month's use of GAC filter

Compounds	GAC-Treated Effluent Concentration ng/L
Pentanal	*
1-Octene	6
Octane	3
Heptanal	4
1-Nonene	11
Nonane	4
Octanal	14
Decane	*
Nonanal	43
p-Methylphenol	*
Decanal	124
Dodecane	*
Undecanal	7
Tridecane	*
Dudecanal	5
Tetradecane	*
Tridecanal	*
Pentadecane	*
Hexachlorobenzene	*
Heptadecane	4
Octadecane	1
Nonadecane	*

*Not quantitated

was interfaced to the mass spectrometer with a glass-lined steel dual-transfer line held at 230°C. Two microlitres of sample in CS_2 were injected with the split closed.[24] The split was opened (20:1 ratio) after 30 s. Grob's hot needle technique[23] (Figure 5) was used for injection of all samples and standards.

The helium carrier gas flow rate was about 3 mL/min at 25°C; the linear velocity was 25 cm/s with a helium head pressure (no flow controller) of 138 kPa (20 psi). The injector was maintained at 260°C. The column temperature program was 20°C isothermal (cooled with liquid nitrogen) for approximately 8 min, then 2°C/min to 250°C. Mass spectra were acquired at the rate of one every 2 s from 14–450 amu at 70 eV and 90°C source temperature. Approximate source pressure was 6.6×10^{-4} Pa (5×10^{-6} torr).

For a typical $(GC)^2$-MS analysis of this type, 3900 scans are recorded (130 min from injection to termination). Identifications were confirmed by comparison of GC and GC-MS properties with those of authentic standards or library spectra from HERL's quantitation library of 215 standard spectra of compounds. This spectral library represents compounds typically detected by Grob CLSA of various drinking water supplies.

Quantitation. Automatic computerized quantitation procedures based on the internal standard method of quantitation were refined and used to calculate the level of organic contaminants and standard compounds in water.[25] Computer procedures using quantitation of a single ion and the total number of ions in a mass spectrum were used and compared. All relative retention time (RRT) information and concentration levels were referenced to the 1-chlorododecane internal standard that was initially spiked into the water samples at 52 ng/L. The quantitation formula used by the computer is

$$\text{amount} = \frac{\text{area} \times \text{internal standard amount}}{\text{internal standard area} \times \text{response factor}} \quad (1)$$

where

$$\text{response factor} = \frac{\text{area} \times \text{internal standard amount}}{\text{amount} \times \text{internal standard area}} \quad (2)$$

Blanks. Since many organics in water can be measured at concentrations of 5 ng/L or less with CLSA, it is critical to incorporate procedural blanks into the analytical scheme. Before actual samples of drinking water were analyzed, filter blanks and CLSA blanks of low-organic water* containing the same internal standard mix were performed. When water is spiked with low levels of organic chemicals for recovery studies, it is necessary to consider the background level of these chemicals in the spiking medium for correct quantitation results. Blank water samples were run between runs of highly contaminated environmental samples, and when a series of samples was analyzed the least contaminated sample was run first.

*Milli-Q®, Millipore Corp., Bedford, Mass.

Recovery studies. Standard mixtures of compounds at the 10–100 ng/L level were prepared in CS_2 and in acetone. The CS_2 standards were used for direct injection into the $(GC)^2$-MS to establish RRT and response factors for individual compounds. For this study ten repetitive injections of the same standard solution were made and the averages of RRT values and response factors for each compound were put into and stored in a computerized quantitation library. The acetone standards were used for spiking directly into the water. These standards were usually made four times the level of the CS_2 standards because only one-fourth of the final CS_2 extract of the carbon filter (2 μL of 8 μL) was used for GC or GC-MS analysis. The recovery data reported later in this paper are the results of 16 purges of the same standard solution spiked in a different 3.8 L (1.0 gal) of blank water before each analysis. Relative retention times and response factors are referenced to 1-chlorododecane. The recovery for each compound was determined by comparing the computer-quantitated amounts from the purged sample with the calculated amounts in the spike according to

$$\text{percent recovery} = \frac{\text{amount found (ng/L)}}{\text{amount spiked (ng/L)}} \times 100 \quad (3)$$

Applications

Monitoring. Figure 6, a GC-FID chromatogram of a drinking water sample injected after CLSA, shows the large

TABLE 2B
Compounds prominent in one GC-MS analysis but not the other after one month's use of GAC filter

Compounds	Influent concentration ng/L
1,2-Dichloropropane	21
1-Pentene	*
1,1,2-Trichloroethane	*
Ethoxy-2-methylpropane	*
Dichloroiodomethane	35
1,1,1-Trichloro-2-propanone	*
Bromoform†	0.8
Bromochloroiodomethane	*
1,3-Dichlorobenzene	*
1,2,3-Trichlorobenzene	1
Chloroform†	34
Bromodichloromethane†	33
Dibromochloromethane†	18

*Not quantitated
†μg/L

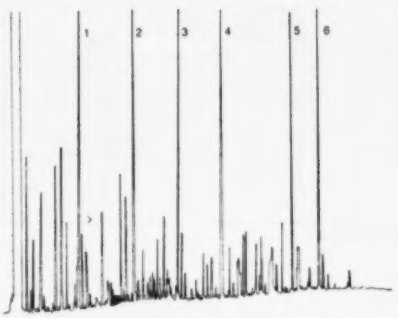

Figure 6. GC–FID chromatogram of a tap water sample after Grob CLSA. Numbered peaks are internal standards: (1) 1-chlorohexane, (2) 1-chlorooctane, (3) 1-chlorodecane, (4) 1-chlorododecane, (5) 1-chlorohexadecane, and (6) 1-chlorooctadecane.

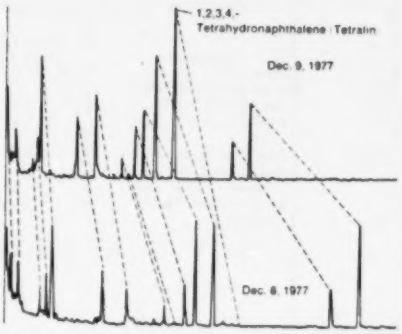

Figure 7. GC–MS profiles of Cincinnati tap water on two consecutive days. Note the sudden appearance of tetralin on December 9, 1977.

number of compounds and the excellent resolution of components achieved by $(GC)^2$. CLSA with $(GC)^2$ is one of the best qualitative tools that HERL has used for measuring organics in drinking waters. Besides measuring large numbers of compounds, CLSA with $(GC)^2$ provides water utility personnel the capability of reproducibly monitoring water on a day-to-day basis for purposes of assessing treatment processes or observing water changes caused by spills or other factors. For example, Figure 7 shows $(GC)^2$–MS profiles of Cincinnati tap water on two consecutive days. In the development stages of HERL's CLSA methodology, it was common to analyze HERL tap water samples at least twice a day. Not only were reproducible profiles obtained, but CLSA was demonstrated to be a valuable monitoring aid for detecting daily changes in organic chemical contamination of a drinking water supply. In this case, the tetralin level showed a very considerable increase in one day, indicating a spill on the Ohio River.

Analysis in support of epidemiological studies. As discussed earlier, one of the main objectives of HERL (exposure evaluation branch) is to validate sensitive methods for measuring organics in drinking water in support of epidemiology. During the past two years the laboratory has often been called on to provide CLSA of contaminated waters exposing populations to known, unknown, or unique problems. Such problems have included taste and odor in a school drinking water causing children to become ill; excessive use of disinfectants (chlorine and chlorine dioxide) in a small community; and high levels of benzene (9 mg/L) in a well water supply to a small factory. Some serious taste and odor problems resulting from chemical contamination at the ng/L (ppt) level go unsolved because methods other than CLSA may not have the capability to detect these low levels or to measure a wide range of organics. HERL is also curently using CLSA to study the reaction products of alternative disinfectants such as chlorine dioxide, ozone, chlorine, and chloramine.

Granular activated carbon evaluation. CLSA has been used to study the effect of GAC on the removal of organic contaminants (industrial contaminants and those produced by the disinfection process) from drinking water. In addition, a pilot study at the local water utility has been in progress over the past few months to determine when GAC should be used, reactivated, or replaced. Tables 1 and 2 show results of CLSA of GAC influents and effluents on initial startup and after one month of study, using the same GAC filter. "Time zero" represents one day of contactor time after 3.8 ML (1 mil gal) of water have passed through the filter. "Time one month" represents 38 days of operation and about 144 ML (38 mil gal) of water through the filter.

The recovery efficiencies for trihalomethanes are very low (4–12 percent) when CLSA is used; therefore, the amounts listed in the tables are approximate. Recovery seems to increase as the bromine content in the molecule increases. Bellar's purge-and-trap method[2,3] gives more accurate results for this class of compounds. As shown in Table 2, after one month's use the GAC filter was doing an adequate job of removing contaminants. However, the table also indicates that other compounds in the GAC-treated effluent may have been generated on the carbon. Such analytical data make CLSA a valuable tool in the support of anticipated organic contaminant control regulations.

Recovery studies. To obtain statistical information on the Grob technique as used by HERL, a study was conducted in which ten repetitive direct injections of a mixture of standard compounds in CS_2 were made on the $(GC)^2$-MS. The same compounds were subsequently added as a mixture to water of low organic content, purged by CLSA, and analyzed by $(GC)^2$-MS to determine their recovery efficiencies. The compounds used for this study are listed in Table 3.

Statistical computations. Statistical computations to determine standard deviations were performed on relative retention times, GC peak areas, response factors, amounts, and recovery efficiencies. Computations for both total ion and single ion quantitation were compared. Greater qualitative and quantitative accuracy was achieved by single ion quantitation for complex environmental samples having coeluting GC peaks. Table 3 shows the results of statistical computations of the repetitive direct injections with quantitation results

TABLE 3

Statistical computations of repetitive direct injection study with quantitation based on a single ion

Compound	Quantitation Mass—m/e	Relative Retention Time (RRT)*	Area*	Amount* ng
Bis-(2-chloroethyl) ether	93	0.525 ± .001	125 339 ± 20 978	61.0 ± 3.1
1,4-Dichlorobenzene	146	0.557 ± .001	174 043 ± 21 770	50.0 ± 4.6
2-Ethyl-1,4-dimethylbenzene	119	0.635 ± .001	231 704 ± 30 954	42.8 ± 3.4
1,2,4-Trichlorobenzene	180	0.728 ± .001	183 366 ± 22 306	72.6 ± 6.5
Hexachloro-1,3-butadiene	225	0.776 ± .000	79 039 ± 8047	84.0 ± 9.6
1-Chlorododecane (I.S.)	91	1.000 ± .000	37 512 ± 7667	52.0 ± 0.00
2,2',4,5,5'-Pentachlorobiphenyl	254	1.447 ± .002	17 564 ± 1505	50.0 ± 7.1

*Average value ± standard deviation, based on 10 injections

TABLE 4

Statistical computations of repetitive direct injection study quantitation amounts: single ion versus total ions

Compound	Quantitation Amount*—ng	
	Single Ion	Total Ions
Bis-(2-chloroethyl) ether	61.0 ± 3.1	61.0 ± 2.2
1,4-Dichlorobenzene	50.0 ± 4.6	50.0 ± 2.7
2-Ethyl-1,4-dimethylbenzene	42.8 ± 3.4	42.8 ± 2.0
1,2,4-Trichlorobenzene	72.6 ± 6.5	72.6 ± 4.0
Hexachloro-1,3-butadiene	84.0 ± 9.6	84.0 ± 5.8
1-Chlorododecane (I.S.)	52.0 ± 0.0	52.0 ± 0.0
2,2',4,5,5'-Pentachlorobiphenyl	50.0 ± 7.1	50.0 ± 3.8

*Average values ± standard deviation, based on 10 injections

TABLE 5

Statistical computations of repetitive purge study with quantitation based on a single ion

Compound	Standard Amount ng/L	Recovered Amount* ng/L	Range ng/L	Recovery Efficiency* percent
Bis-(2-chloroethyl) ether	21.5	0.1 ± 0.1	0-0.2	0.4 ± 0.3
1,4-Dichlorobenzene	20.2	14.4 ± 3.8	9.1-20.8	71.2 ± 18.9
2-Ethyl-1,4-dimethylbenzene	13.6	10.4 ± 2.5	7.5-15.1	76.6 ± 18.6
1,2,4-Trichlorobenzene	18.8	10.4 ± 2.6	6.6-13.6	55.1 ± 14.0
Hexachloro-1,3-butadiene	21.9	19.6 ± 3.6	12.9-31.2	89.4 ± 25.7
1-Chlorododecane (I.S.)	52.0	41.9 ± 15.4	19.4-70.5	80.6 ± 29.5
2,2',4,5,5'-Pentachlorobiphenyl	21.4	4.0 ± 1.6	1.4-6.7	18.8 ± 7.5

*Average value ± standard deviation, based on sixteen purges

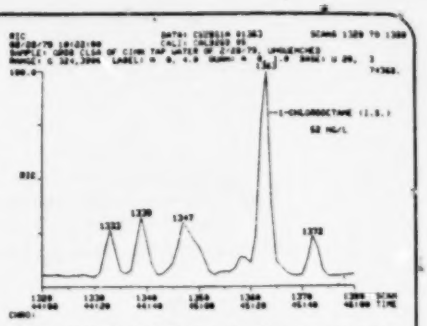

Figure 8. Partial RGC showing overlapping GC peaks at scan 1347

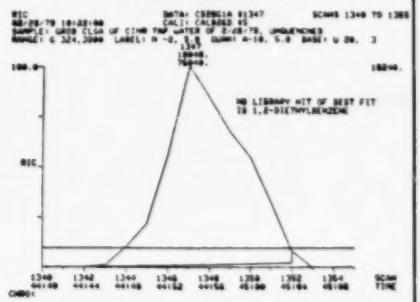

Figure 9. RGC expanded to emphasize scan 1347. Second number above apex of peak is the peak height; number below it (76040) is the area representing total ions.

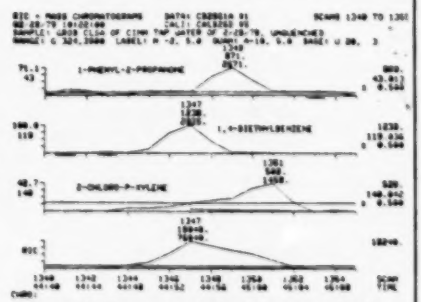

Figure 10. Example of single ion quantitations (areas) to resolve the effects of overlapping and coeluting GC peaks. Lower numbers above apex of peaks in the top three profiles (43, 119, and 140, respectively) represent the areas of the specific ions.

based on a single ion. Note the excellent reproducibility of the relative retention time data. This table indicates that peak areas vary an average of 13 percent whereas the amounts vary an average of 9 percent. Since the sensitivity of the mass spectrometer fluctuates daily, these area variations are expected. However, the internal standard method of quantitation compensates for these changes when the amounts are calculated by the computer.

Table 4 shows a comparison of amounts quantitated by a single ion and by total ions. It appears that both methods work equally well, with total ions having a slight edge on standard deviations. The amounts under a single ion vary an average of ± 9 percent whereas the amounts under total ions vary an average of ± 5 percent. This is true only when very clean mixtures such as standards are used. The resolving power of $(GC)^2$ greatly complements total ion quantitation. The authors have noted also that the individual response factors calculated from total ion quantitation do not vary as much as those for single ion quantitation. Single ion quantitation was recently discussed by Coleman.[28]

Figures 8-10 demonstrate the advantages of single ion versus total ion quantitation of components in a contaminated water supply. Figure 8 shows a partial reconstructed gas chromatogram (RGC) emphasizing scan 1347 to show the effects of overlapping GC peaks. Figure 9 shows the results of quantitation (area) by total ions. A computer search of the spectral library for a mass spectrum matching the unknown selected 1,2-diethylbenzene as the best fit. Figure 10 shows that the GC peak at scan 1347 was composed of at least three compounds and that by quantitating on distinct single ions (43, 119, and 140 appearing on the y axis) accurate identifications and quantitative results were achieved.

An average of 200 to 300 organic compounds are identified in most drinking water samples using Grob CLSA and $(GC)^2$-MS. Even though most laboratories use WCOT $(GC)^2$ for CLSA samples, it is possible to use packed GC columns and conventional GC detectors such as flame ionization detectors (FID) and electron capture detectors (ECD). The

most cost-effective instrumental approach to CLSA samples is the use of $(GC)^2$ with the column effluent split between flame ionization and electron capture detectors and the use of automated GC quantitation data systems. $(GC)^2$-MS is still required for periodic confirmation studies.

Table 5 shows the recovery efficiencies for each compound and its standard deviation. The data indicate that all compounds do not have the same recoverability, primarily because of differences in water solubility and vapor pressure. With the exceptions of bis-(2-chloroethyl) ether and 2,2',4,5,5'-pentachlorobiphenyl, all compounds were purged moderately well from the water, with an average recovery efficiency of 75 percent and an average standard deviation of 22 percent. Because of the amounts spiked in water for this study (13.6–21.9 ng/L), this may be a worst case: higher spikes should increase recovery efficiencies.

The low recovery efficiencies for bis-(2-chloroethyl) ether and the pentachlorobiphenyl isomer are not disappointing. The ether was added to this ongoing study with its numerous compounds[25] because of its toxicity and because of its occurrence in a few major United States water supplies. Detection of this compound in drinking water at low levels by CLSA means a much higher level of human exposure. The recovery of pentachlorobiphenyl is admirable. The authors have not detected this compound in water using CLSA, but its recovery suggests the range (MW 324) and type of compounds measurable by CLSA.

Summary and conclusions

Grob CLSA has proved to be an excellent analytical tool for monitoring organics in water at the ng/L (ppt) level, and to be invaluable in support of epidemiology, for studying uses and effects of alternative disinfectants, and for GAC evaluation at bench or plant scale. Its use, in conjunction with $(GC)^2$-FID or $(GC)^2$-MS, can provide daily profiles of water quality. CLSA with $(GC)^2$-MS can also be used to provide very reproducible RRT data for automatic quantitation procedures. $(GC)^2$-MS quantitation by total ions and by single ion methods was shown to be equally accurate when standard mixtures were used or samples had well-resolved GC peaks, although it was found to be advantageous to quantitate on single ions when identifications of organics in complex (highly contaminated) water samples were being confirmed. The recovery efficiency of five of seven compounds purged from water averaged 75 ± 22 percent standard deviation overall. Comparison of Grob CLSA with other trace organic methods was recently discussed by Melton.[27]

In conclusion, Grob CLSA with $(GC)^2$-MS can be used for qualitative and quantitative analysis of organics in water at the low ng/L level, provided that internal standards are incorporated into the analysis and recovery data are available for all compounds of interest.

References

1. Grob, K. Organic Substances in Potable Water and in its Precursor, Part 1. Methods for Their Determination by Gas-Liquid Chromatography. *Jour. Chromatogr.*, 84:255 (1973).
2. Bellar, T.A. & Lichtenberg, J.J. Determining Volatile Organics at Microgram-Per-Litre Levels by Gas Chromatography. *Jour. AWWA*, 66:12:739 (Dec. 1974).
3. Bellar, T.A.; Lichtenberg, J.J.; & Kroner, R.C. The Occurrence of Organohalides in Chlorinated Drinking Waters. *Jour. AWWA*, 66:12:703 (Dec. 1974).
4. Kopfler, F.C. et al. GC/MS Determination of Volatiles for the National Organics Reconnaissance Survey (NORS) of Drinking Water. *Identification and Analysis of Organic Pollutants in Water* (Lawrence H. Keith, editor). Ann Arbor Sci. Pub. Inc., Ann Arbor (1976).
5. Coleman, W.E. et al. The Occurrence of Volatile Organics in Five Drinking Water Supplies Using Gas Chromatography/Mass Spectrometry. *Identification and Analysis of Organic Pollutants in Water* (Lawrence H. Keith, editor). Ann Arbor Sci. Pub. Inc., Ann Arbor (1976).
6. Lingg, R.D. et al. Quantitative Analysis of Volatile Organic Compounds by GC-MS. *Jour. AWWA*, 69:11:605 (Nov. 1977).
7. Grob, K. & Zürcher, F. Stripping of Trace Organic Substances from Water. Equipment and Procedure. *Jour. Chromatogr.*, 117:285 (1976).
8. White, L.D. et al. A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere. *Jour. Amer. Ind. Hyg. Assn.*, 31:225 (1970).
9. Grob, K. & Grob, G. Organic Substances in Potable Water and in its Precursor, Part 2. Applications in the Area of Zürich. *Jour. Chromatogr.*, 90:303 (1974).
10. Grob, K.; Grob, K. Jr.; & Grob, G. Organic Substances in Potable Water and in its Precursor, Part 3. The Closed-Loop-Stripping Procedure Compared With Rapid Liquid Extraction. *Jour. Chromatogr.*, 106:299 (1975).
11. Stieglitz, L. et al. The Behavior of Organohalides in the Treatment of Drinking Water. *Vom Wasser*, 47:347 (1976).
12. Zürcher, F. & Giger, W. The Study of Volatile Organic Compounds in the Glatt River. *Vom Wasser*, 47:37 (1976).
13. Giger, W. et al. Analysis of Organic Constituents in Water by High Resolution Gas Chromatography in Combination with Specific Detection and Computer-Assisted Mass Spectrometry. *Identification and Analysis of Organic Pollutants in Water* (Lawrence H. Keith, editor). Ann Arbor Sci. Pub. Inc., Ann Arbor (1976).
14. Giger, W.; Molnar-Kubica, E.; & Wakeham, S. Volatile Chlorinated Hydrocarbons in Ground and Lake Water. *Aquatic Pollutants* (O. Hutzinger, editor). Pergamon Press, Oxford (1976).
15. Schwarzenbach, R.P. et al. Distribution, Residence Time, and Fluxes of Tetrachloroethylene and 1,4-Dichlorobenzene in Lake Zurich, Switzerland. *Environ. Sci. Technol.*, 13:11:1367 (Nov. 1979).
16. Giger, W. Inventory of Organic Gases and Volatiles in the Marine Environment. *Marine Chem.*, 5:429 (1977).
17. Schwarzenbach, R.P. et al. Volatile Organic Compounds in Coastal Seawater. *Organ. Geochem.*, 1:93 (1978).
18. McCarty, P.L.; Reinhard, M.; & Argo, D.G. Organics Removal by Advanced Wastewater Treatment. Proc. 97th AWWA Annual Conf., Anaheim, Calif. (May 1977).
19. Reinhard, M. et al. Trace Organics Removal by Advanced Waste Treatment. Proc. ASCE, 105:EE4:14760 (Aug. 1979).
20. Reinhard, M. et al. Specific Compound Analysis by Gas Chromatography and Mass Spectroscopy in Advanced Treated Waters. NATO/CCMS Conf. on Practical Application of Adsorption Techniques. Reston, Va. (May, 1979).
21. McCarty, P.L. & Reinhard, M. Statistical Evaluation of Trace Organics Removal by Advanced Wastewater Treatment. WPCF Annual Conf., Anaheim, Calif. (Oct. 1979).
22. McCarty, P.L.; Argo, D.; & Reinhard, M. Operational Experiences with Activated Carbon Adsorbers at Water Factory 21. *Jour. AWWA*, 71:11:683 (Nov. 1979).
23. Grob, K. & Grob, K. Jr. Splitless Injection and the Solvent Effect. *Jour. HRC+CC*, 1:1:57 (July 1978).
24. Grob, K. & Grob, K. Jr. Isothermal Analysis on Capillary Columns Without Stream Splitting. The Role of the Solvent. *Jour. Chromatogr.*, 94:53 (1974).
25. Grob, K. & Grob, G. Practical Capillary Gas Chromatography—a Systematic Approach. *Jour. HRC+CC*, 2:3:109 (Mar. 1979).
26. Coleman, W.E. et al. Automatic Quantitation and Statistical Evaluation of Organic Contaminants Using a Computerized Glass Capillary Gas Chromatography/Mass Spectrometer System ($(GC)^2$/MS/DS) and Grob Closed-Loop Stripping. Presented at the Second Chemical Congress of the North American Continent, Las Vegas, Nev. (Aug. 24–29, 1980).
27. Melton, R.G. et al. Comparison of Grob Closed-Loop Stripping Analysis (GCLSA) to Other Trace Organic Methods. Presented at the Second Chemical Congress of the North American Continent, Las Vegas, Nev. (Aug. 24–29, 1980).

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